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(54) OLIGOMERISATION AND CO OLIGOMERISATION CATALYSTS

(71) We, AKADEMIE DER WISSENSCHAFTEN DER DDR OF RUDOWER CHAUSSE, Berlin, German Democratic Republic, a Corporation organised under the laws of the German Democratic Republic, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with a process for the production of heterogeneous catalysts suitable for the oligomerisation and co-oligomerisation of olefins, which catalysts have a good selectivity and a high activity.

It is known that olefins, especially propene, can be oligomerised with the help of solid catalysts which, as catalytically active components, contain cobalt or nickel or the oxides thereof. As carrier material, there are used various activated charcoals, aluminosilicates, optionally with the admixture of magnesium oxide, as well as aluminium oxides and zeolites. However, even when using comparatively high pressures and temperatures, the activity is scarcely satisfactory.

It is also known that aluminium oxide, silicon dioxide or aluminosilicate carriers which have been impregnated with a divalent nickel salt and a complex former or with monovalent nickel complexes and subsequently treated with an organo-aluminium compound or with an organo-metallic alkylating agent, can also be used to oligomerise olefins. Because of the low reactivity of these catalysts, it is necessary to use increased pressures and comparatively long reaction times.

Another group of known heterogeneous oligomerisation catalysts contain alkali metals as effective components. As carriers, there are used magnesium silicates, magnesium oxide, aluminium oxide, potassium carbonate,

activated charcoal or graphite, on to which are deposited the alkali metals or their hydrides or organo compounds, in finely-divided form. Since the activity of the catalysts thus obtained is low, they can also only be used at high pressures and reaction temperatures and with long residence times.

It is an object of the present invention to provide heterogeneous oligomerisation catalysts for olefins which do not suffer from the above-mentioned deficiencies and disadvantages and which show, under normal conditions, a high activity and good selectivity.

Thus, according to the present invention, there is provided a process for the production of heterogeneous oligomerisation and co-oligomerisation catalysts for olefins, wherein a completely hydrated aluminium hydroxide or a partially dehydrated aluminium hydroxide or hydroxide group-containing aluminium oxide carrier material is first thermally pre-treated, then reacted with at least one halogen-containing organo-aluminium compound and subsequently impregnated with at least one divalent nickel and/or divalent cobalt complex in which ligand atoms include oxygen, nitrogen, phosphorus, arsenic and/or antimony, the reaction and subsequent impregnation being carried out at a temperature of -50 to 150°C. and preferably of 0 to 60°C.

If desired, a divalent nickel and/or cobalt complex can be used in which one or two coordination positions of the central atom is occupied by an imino nitrogen atom.

As carrier materials, there can be used, for example, bayerite, hydrargillite, böhmite and γ -aluminium oxide.

For the reaction with the thermally pre-treated carrier materials, there can be used, for example, halogen-containing organo-

[Price 33p]

103 Ni

aluminium compounds of the general formula



wherein X is a fluorine, chlorine, bromine or iodine atom and R is an alkyl, cycloalkyl, alkenyl, cycloalkenyl, aryl, aralkyl or aralkenyl radical, triethyl aluminium sesquichloride or diethyl aluminium chloride being preferably used.

The reaction advantageously takes place in the temperature range of -50 to 100°C . and preferably at about 0°C ., whereby, for 30 ml. of carrier material, there are used 20–50 ml. of halogen-containing organo-aluminium compound. The halogen-containing organo-aluminium compound can be applied to the carrier in indiluted form or dissolved in an inert solvent. As solvent for the halogen-containing organo-aluminium compounds, there can be used, for example, not only aliphatic but also aromatic halogenated hydrocarbons, as well as pure aromatic, aliphatic or cycloaliphatic hydrocarbons.

The thermally pre-treated carrier materials reacted with the halogen-containing organo-aluminium compounds are loaded with divalent nickel and/or divalent cobalt complexes. As solvents, there can here also be used the above-mentioned hydrocarbons or halogenated hydrocarbons.

As divalent nickel complexes, there can be used, for example, bis - (salicylidene - iminato) nickel, bis - (N - n - butyl - salicylidene - iminato) nickel, bis - (N - n - dodecylsalicylidene - iminato) nickel, bis - (N - cyclohexyl - salicylidene - iminato) nickel, bis - (N - phenyl - salicylidene - iminato) nickel, bis - (N - o - chlorophenyl - salicylidene - iminato) nickel, bis - N - o - pyridyl - salicylidene - iminato) nickel, bis - (2 - aminobenzylidene - iminato) nickel, bis - [(N - n - butyl) - 2 - aminobenzylidene - iminato] nickel, bis - [(N - phenyl) - 2 - aminobenzylidene - iminato] nickel, bis - [(N - o - pyridyl) - 2 - aminobenzylidene - iminato] nickel, bis - [(N - n - butyl) - 2 - diphenylphosphine - benzylidene - iminato] nickel, bis - [(N - phenyl) - 2 - diphenylarsino - benzylidene - iminato] nickel, bis - (2 - pyrrolidene - iminato) nickel, bis - [(o - chlorophenyl) - 2 - pyrrolidene - iminato] nickel, bis - (2 - hydroxy - azobenzene) nickel, [(N - β - hydroxyethyl) - salicylidene - iminato] nickel, [(N - o - hydroxyphenyl) - salicylidene - iminato] nickel, [(N - β - methylaminoethyl) - 2 - pyrrolidene - iminato] nickel, 2,2' - dihydroxyazobenzene nickel, N,N' - bis - (salicylidene) - ethylenediamino nickel, N,N' - bis - (salicylidene) - o - phenylenediamino nickel, N,N' - bis - (o - aminobenzylidene) - ethylenediamine nickel, N,N' - bis - (2 - pyrrolidene) - o - phenyldiamino nickel, N,N' - bis - (2 - pyrrolidene) -

1,2 - diphenyl - ethylenediamino nickel and nickel acetyl acetonate, as well as the complex formed between nickel acetyl acetonate and triphenyl phosphine.

In the same way, there can also be used the corresponding divalent cobalt complexes.

Furthermore, mixtures of divalent nickel and/or divalent cobalt complexes can be used.

The divalent nickel complexes can, in general, be prepared quickly and simply and are easy to purify. The o -substituted arylaldehyde or arylketimine nickel complexes, for example, the salicylaldehyde, o -aminobenzaldehyde, pyrrole - α - aldehyde or o - hydroxyacetophenoneimine nickel complexes can be obtained by reacting a slight excess of primary amine in a polar solvent, such as ethanol or a halogenated aliphatic hydrocarbon, with the bis - o - hydroxy- or bis - o - aminobenzaldehyde or bis - o - hydroxy- or bis - o - aminoaryl ketone nickel complex. The metal ion can also be homogeneously reacted in aqueous or alcoholic solution with the appropriate Schiff base in the presence of hydroxyl or acetate ions or ammonia. The crude products can be recrystallised from an appropriate alcohol or from an aromatic hydrocarbon.

The o -hydroxyazobenzene nickel complexes, which can be derived from the corresponding o - hydroxyphenolazomethines by replacement of the methine group thereof by a nitrogen atom, are also easily obtainable. The organic components of these complexes have been known for a long time as dyestuffs and are thus large-scale products which can be reacted in a simple manner with nickel hydroxide or nickel salts and ammonia to give the corresponding di- or trichelates and which can be obtained in pure form by crystallisation. In the same way as the o -hydroxy- and similarly to the o -aminobenzaldehydes, the o -amino and o -pyrrole-azo compounds give poly-chelate divalent nickel complexes. The production thereof does not differ fundamentally from that of the other complexes mentioned.

The divalent cobalt complexes can be produced in an analogous manner but, in this case, it is necessary to work under an atmosphere of inert gas.

The catalysts can be very easily regenerated. Thus, a thermally inactivated catalyst can again be impregnated with a divalent nickel or cobalt complex and subsequently with a small amount of a halogen-containing organo-aluminium compound.

A slight drop in activity occurring after a comparatively long period of working can easily be compensated merely by applying small amounts of halogen-containing organo-aluminium compound to the catalyst.

The heterogeneous catalysts according to the present invention can be used, for example, for the oligomerisation of ethylene, propene, butene, isoprene and butadiene. Furthermore,

they can be used for carrying out a co-oligomerisation between mono-olefins and between mono- and diolefins.

Heterogeneous catalysts produced according to the present invention for olefins are simple to produce and are based upon cheap carrier materials. They can be used at ambient temperature and atmospheric pressure and exhibit a high reaction velocity and, in many cases, display a good selectivity. A further advantage of these catalysts is their good activity over long periods of time and the ease with which they can be regenerated.

The oligomerisation or co-oligomerisation of the olefins can be carried out in a solid bed reactor. This can consist, for example, of a vertical glass tube, provided with a cooling jacket, with a length of about 30 cm. and a diameter of about 2 cm. with a fused-in glass sinter plate. The packing level of the catalyst, through which the reactants flow from above, can be 10–15 cm., depending upon the carrier material. The carrier material is preferably used with a particle size of 0.3–0.6 mm. The temperature can be measured by means of displaceable thermo-elements. All working steps up to the impregnation of the catalysts should be carried out under argon, the impregnation process itself preferably being complete at a temperature of about 0°C. in an atmosphere of the olefin which is to be oligomerised.

The following Examples are given for the purpose of illustrating the present invention:—

Example 1.

30 g. böhmite are heated to 45°C. within the course of 1 hour, thereafter heated slowly to 110°C. within the course of 6 hours and subsequently maintained at this temperature for 3 hours.

The böhmite thermally pre-treated in this manner is mixed at 50°C., within the course of 3 hours, with a solution of 20 ml. triethyl aluminium sesquichloride in chlorobenzene (1:2). After washing out with chlorobenzene and drying at 40°C., the carrier is impregnated at 0°C. with a solution of 123 mg. bis - (N - n - butyl - salicylideneiminato) nickel in 11 ml. chlorobenzene and subsequently dried at 40°C. Thereafter, the catalyst is treated at 0°C. in an atmosphere of propene, within the course of 1 hour, with 1 ml. triethylaluminium sesquichloride. The propene conversion at 20°C. is 660 v/v.h. Composition of the reaction product:

72% dimers of which 16.5% *n*-hexenes
20% trimers
8% higher oligomers.

Example 2

30 g. böhmite, which has been pre-treated

in the manner described in Example 1, are mixed with 30 ml. of a solution of triethyl aluminium sesquichloride. After drying the carrier at 70°C., it is impregnated at 0°C. with a solution of 124 mg. bis - (N - n - butyl - salicylideneiminato) nickel in 35 ml. *n*-hexane. Subsequently, a mixture of propene and argon (1:1) is allowed to flow through at 0°C. The reaction temperature thereby increases to 45°C., in spite of intensive cooling. The propene conversion at 30°C. is 1000 v/v.h. Composition of the reaction product:

70% dimers of which 27% *n*-hexenes
23.4% trimers
6.6% higher oligomers

The catalyst can be used for several days on end with somewhat reduced effectiveness. If it is stored in an atmosphere of argon, then, even after several weeks, it can still be activated with a small amount of triethyl aluminium sesquichloride to give the initial degree of activity.

Example 3

The böhmite catalyst according to Example 2, inactivated due to an increased reaction temperature, is impregnated with 62 mg. bis - (N - n - butyl - salicylideneiminato) nickel in 50 ml. *n*-hexane, activated with 0.25 ml. triethyl aluminium sesquichloride and again used for the conversion of propene. The propene conversion at 30°C. is 1000 v/v.h. Composition of the reaction product:

52% dimers of which 10.8% *n*-hexenes
32% trimers
15% higher oligomers.

Example 4.

30 g. bayerite are continuously heated to a temperature of 95°C. within the course of 4 hours. Thereafter, it is maintained at this temperature for a further 3 hours. The bayerite thermally pre-treated in this manner is mixed with a solution of 40 ml. triethyl aluminium sesquichloride, care being taken that the temperature does not exceed 20°C. In the course of 5 hours, the catalyst bed is dried at a temperature of up to 30°C. After impregnation with a solution of 250 mg. bis - (N - n - butyl - salicylidene - iminato) nickel in 80 ml. *n*-hexane, the catalyst obtained is used for the conversion of propene. The propene conversion at 50°C. is 2000 v/v.h. Composition of the reaction product:

60–65% dimers of which 20–24% *n*-hexenes
21–25% trimers
10–19% higher oligomers.

The catalyst has an outstandingly pro-

- longed activity which remains substantially constant over the course of several days. If, after use and drying, the catalyst is stored in an atmosphere of argon, then it can be used again after quite a long time, without a reduction of activity.
- 63% dimers of which 19% *n*-hexenes
26% trimers
11% higher oligomers. 60

In the case of operating at 65°C., the reaction product had the following composition:

- Example 5**
30 g. of the bayerite thermally treated and mixed with triethyl aluminium sesquichloride according to Example 4 are impregnated with a solution of 155 mg. nickel acetyl acetonate in 30 ml. toluene and subsequently washed out with 100 ml. toluene. Activation takes place with triethyl aluminium sesquichloride, which is introduced together with the propene which is to be oligomerised. For this purpose, the propene flows through a wash bottle containing triethyl aluminium sesquichloride which is inserted directly before the reaction. The propene conversion at 45°C. after 5 hours is 1330 v/v.h. Composition of the reaction product:
- 71.5% dimers of which 25.8% *n*-hexenes
23.0% trimers
5.5% higher oligomers 65

The propene conversion is 650 v/v.h.

- Example 8**
The bayerite catalyst according to Example 4 is used for the oligomerisation of ethylene. The ethylene conversion at 55°C. is 2000 v/v.h. (a).
After throttling the supply of ethylene to an ethylene conversion of 1500 v/v.h. (b) or to 1000 v/v.h. (c) at 40°C., the reaction products obtained have the following compositions:
- 70
75

- 61% dimers of which 20% *n*-hexenes
25% trimers
14% higher oligomers. 25
- a)
55% butenes
35% hexenes of which 15% *n*-hexenes
10% higher oligomers, preponderantly octenes 80

- Example 6**
Bayerite thermally pre-treated and mixed with triethyl aluminium sesquichloride according to Example 4, is reacted at 0°C., in an atmosphere of propene, with a mixture of 1 mMol nickel acetyl acetonate and 1 mMol triphenyl phosphine and, after drying at 0°C., activated with 1 ml. triethyl aluminium sesquichloride. The propene conversion at 45°C. is 1100 v/v.h. Composition of the reaction product:
- 29 % butene
19.8% hexenes of which 28% *n*-hexenes
31.1% octenes of which 8.7% *n*-octenes
12.7% decenes
5.8% dodecenes
1.8% tetradecenes 85

- 76% dimers of which 19.1% *n*-hexenes
18% trimers
6% higher oligomers. 35
- b)
15.0% butenes
22.9% hexenes of which 28% *n*-hexenes
28.5% octenes of which 10.5% *n*-octenes
18.5% decenes of which 4% *n*-decenes
10.9% dodecenes
4.2% tetradecenes. 90

- Example 7**
30 g. γ -aluminium oxide are heated within the course of 8 hours, by a continuous increase of temperature, to 450°C. and subsequently maintained for 16 hours at this temperature.
- 100

- The γ -aluminium oxide thermally treated in this manner is mixed at 0°C., in an atmosphere of argon, with 30 ml. triethyl aluminium sesquichloride, heated for 1 hour under argon at 20°C. and then for 2 hours under argon at 30°C.
- 105

- After impregnation with a solution of 125 mg. bis - (N - *n* - butyl - salicylidene - iminato) nickel in 80 ml. hexane, the catalyst obtained is used for the conversion of propene. Propene conversion at 45°C. is 1300 v/v.h. Composition of the reaction product:
- 50% butenes
50% hexenes. 110

When the conversion rate is lowered to 1000 v/v.h. by throttling the supply of ethylene and the temperature of the reactor

is maintained at 30°C., then the reaction product obtained has the following composition:

- 26% butenes
38% hexenes of which 10.5% *n*-hexenes
36% octenes.

Example 10

Bayerite thermally pre-treated and mixed with triethyl aluminium sesquichloride according to Example 4, is impregnated with a solution of 250 mg. bis - (N - *n* - butyl - salicylidene - iminato) cobalt in 35 ml. chlorobenzene and the catalyst obtained is used for the conversion of ethylene.

- Ethylene conversion at 20°C.: 70 v/v.h.
ethylene conversion at 50°C.: 120 v/v.h.
ethylene conversion at 90°C.: 150 v/v.h.

Composition of the reaction product:

- 100% butenes of which 30-50% but-1-ene.

Example 11

Bayerite thermally pre-treated according to Example 4 is mixed with 50 ml. diethyl aluminium chloride. After removing excess organo-aluminium compound, finally by warming to 30°C. in an atmosphere of argon, the carrier is impregnated at 0°C., in an atmosphere of ethylene, with a solution of 160 mg. bis - (N - *n* - butyl - salicylidene - iminato) cobalt in 20 ml. toluene. Subsequently, the catalyst is dried at 0°C. in an atmosphere of argon, the argon first being passed through a wash bottle containing triethyl aluminium sesquichloride. In the temperature range of 10 to 60°C., the catalyst has an ethylene oligomerisation activity of 170 v/v.h. The reaction product obtained consists exclusively of butenes.

Example 12

Bayerite thermally pre-treated and mixed with triethyl aluminium sesquichloride according to Example 4 is impregnated with a solution of 575 mg. bis - (N - *n* - butyl - salicylidene - iminato) cobalt and 41 mg. bis - (N - *n* - butyl - salicylidene - iminato) nickel in 50 ml. chlorobenzene. The ethylene conversion at 10°C. is 200 v/v.h. Composition of the reaction product:

- 9.0% butenes
20.9% hexenes of which 50% *n*-hexenes
15.0% octenes of which 8% *n*-octenes
54.2% decenes of which 3% *n*-decenes
remainder higher oligomers.

WHAT WE CLAIM IS:—

1. Process for the preparation of heterogeneous oligomerisation and co-oligomerisation catalysts for olefins, wherein a completely hydrated aluminium oxide or a

partially dehydrated aluminium hydroxide or a hydroxide group-containing aluminium oxide carrier material is first thermally pre-treated, then reacted with at least one halogen-containing organo-aluminium compound and subsequently impregnated with at least one divalent nickel and/or divalent cobalt complex in which ligand atoms include oxygen, nitrogen, phosphorus arsenic and/or antimony, the reaction and subsequent impregnation being carried out at a temperature of -50 to 150°C.

2. Process according to claim 1, wherein one or two coordination positions of the central atom of the divalent nickel and/or divalent cobalt complex is occupied by an imino nitrogen atom.

3. Process according to claims 1 or 2, wherein the carrier material is bayerite, hydrargillite, böhmite or γ -aluminium oxide.

4. Process according to any of the preceding claims, wherein the thermally pre-treated carrier material is reacted with at least one halogen-containing organo-aluminium compound of the general formula



in which X is a fluorine, chlorine, bromine or iodine atom and R is an alkyl, cycloalkyl, alkenyl, cycloalkenyl, aryl, aralkyl or aralkenyl radical.

5. Process according to any of the preceding claims, wherein the reaction and subsequent impregnation are carried out at a temperature of 0 to 60°C.

6. Process according to any of claims 1 to 4, wherein the reaction with the halogen-containing organo-aluminium compound is carried out at a temperature of -50 to 100°C.

7. Process according to claim 6, wherein the reaction with the halogen-containing organo-aluminium compound is carried out at a temperature of about 0°C.

8. Process according to any of the preceding claims, wherein, for each 30 ml. of carrier material, there are used 20-50 ml. of halogen-containing organo-aluminium compound.

9. Process according to any of the preceding claims, wherein the halogen-containing organo-aluminium compound is used either in undiluted form or dissolved in an inert solvent.

10. Process according to any of the preceding claims, wherein the nickel and/or cobalt complex is applied in the form of a solution in an inert solvent.

11. Process according to claim 9 or 10, wherein the inert solvent is an aromatic, aliphatic or cycloaliphatic hydrocarbon or a halogenated aliphatic or aromatic hydrocarbon.

12. Process according to claim 1 for the

preparation of heterogeneous oligomerisation and co-oligomerisation catalysts, substantially as hereinbefore described and exemplified.

- 5 13. Heterogeneous oligomerisation and co-oligomerisation catalysts, whenever prepared by the process according to any of claims 1 to 11.

- 10 14. Process for the regeneration of a catalyst according to claim 13 which has become thermally inactivated, wherein said catalyst is impregnated with at least one divalent nickel and/or cobalt complex as defined in claim 1 or 2 and subsequently impregnated with a small amount of a halogen-containing organo-aluminium compound.

- 15 15. Process for the reactivation of a catalyst according to claim 13 which has undergone a small drop in activity, wherein a small amount of at least one halogen-containing organo-aluminium compound is applied to said catalyst.

16. Process for the oligomerisation or co-oligomerisation of at least one mono-olefin and/or at least one diolefin, wherein the reaction is carried out with the use of a catalyst 25 according to claim 13.

17. Process of oligomerisation or co-oligomerisation according to claim 16, substantially as hereinbefore described and exemplified. 30

18. Oligomers and co-oligomers, whenever produced by the process according to claim 16 or 17.

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